EFFECTIVE DIPOLE MOMENT PARAMETRS OF XY_2TYPE MOLECULES CALCULATED ON THE BASIS OF ISOTOPIC SUBSTITUTION THEORY

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РАСЧЕТ ПАРАМЕТРОВ ЭФФЕКТИВНОГО ДИПОЛЬНОГО МОМЕНТА МОЛЕКУЛ ТИПА XY_2 НА ОСНОВЕ ТЕОРИИ ИЗОТОПОЗАМЕЩЕНИЯ

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Аннотация. *На основе теории изотопозамещения были получены соотношения, позволяющие рассчитать параметры эффективного дипольного момента изотопологов молекул типа XY_2 при симметричном замещении атомов. Исходной информацией, необходимой для осуществления подобных расчетов, является информация о структурных параметрах и параметрах эффективного дипольного момента «материнской» молекулы. Полученные результаты справедливы для комбинационных полос и обертонов. Полученные соотношения значительно упрощают, а в некоторых случаях, делают возможным процесс определения абсолютных интенсивностей линий поглощения изотопологов типа XY_2.*

Introduction. In the last decades, high-resolution molecular spectroscopy has been increasingly concerned with the study of vibration-rotation line intensities. The reason for this fact is the necessity of having the best line intensities in order to extract the maximum of information from remote sensing experiments in the field of atmospheric physics and for interpreting astrophysical and combustion data. Nowadays in most cases, line intensities of the “parent” molecules (the most abundant isotopologue) are obtained with high accuracy. Nevertheless despite the large need in high-precision quantitative information about line intensities of different isotopologues for numerous problems, up to now, the number of corresponding researches is much less than the number of studies of “parent” species. The main reason is that in such studies, in addition to the total pressure in the sample, it is necessary to know the partial pressure of the studied isotopologue with high precision [1]. The latter, in the overwhelming majority of cases, is impossible due to the intense exchange of atoms of different isotopes in the sample. The method of determining the partial pressure in a gas mixture was developed earlier [2]. The main requirement of that method is the necessity to know effective dipole moment parameters of the studied isotopologue. Unfortunately, this information is absent in the literature in most of the cases. Thus, the main goal of the present study is to derive relations allowing to obtain the effective dipole moment parameters of the studied isotopologue on the basis of information about the «parent » species which is known with the high accuracy usually. These parameters may be used to apply the method of determining the partial pressure in a gas mixture in the spectral region where combination bands and overtones are located. Also these

parameters are the main contributions to the expansion of the effective dipole moment on normal coordinates, so they may be used as a rough estimation of the effective dipole moment of the studied isotopologue.

Theoretical background. Line intensities require the calculation of the vibration-rotation matrix elements of the transformed dipole moment operator [3]. Thereby the purpose of this study is to present the new theoretical treatment that can be used to set up the transformed dipole moment operator of isotopologues of XY_2 type molecules.

Since the vibration-rotation energies and wavefunctions are generally calculated using transformed Hamiltonians, it is necessary to use a transformed dipole moment operator to calculate transition moments correctly:

$$\mu_z^{'} = G^{+} P_z G \ ,$$

where G is a unitary ro-vibrational operator [2] and $P_z$is a dipole moment operator, which can be written as

$$P_z = \sum_{\alpha} k_{Z\alpha} \left\{ \mu_\alpha^e + \sum_{\lambda} \mu_\alpha^\lambda Q_\lambda + \sum_{\lambda\nu} \mu_\alpha^{\lambda\nu} Q_\lambda Q_\nu + \ldots \right\} .$$

Here $k_{Z\alpha}$ are elements of the direction cosines matrix, μ_α^e - permanent dipole moment of “parent” molecule, Q_λ are dimensional normal coordinates, μ_α^λ and $\mu_\alpha^{\lambda\nu}$ are parameters of the dipole moment operator. Using the isotopic substitution theory (for more details see Ref. [4]) it is possible to obtain the set of general relations, which associate transformed dipole moment parameters of isotopologue with available in the literature, as a rule, information on the transformed dipole moment parameters of “parent” molecule.

Results and discussion. In the present study only XY_2 type molecules and theirisotopologues were considered. In particular, if one considers only isotopologues isomorphic to the C_{2v} point symmetry group and takes into account symmetry properties, final relations will take much more simple form.In Table 1 the calculated values of transformed dipole moment parameters for $H_2{}^{18}O$ molecules are represented. As it could be seen from Table 1, the obtained results are ingood agreement with the data available in the literature. Therefore, it can be concluded that the obtained formulas are correct and can be used for further calculations.

Table 1

The coefficients of the expansion of the transformed dipole moment operator with respect to normal coordinates of $H_2{}^{18}O$ (all values are in Debye)

	This work	Exp.
$^{22}\mu_x$	0.00553	0.00565[a]
$^{12}\mu_x$	-0.00219	-0.00219[b]
$^{23}\mu_z$	0.02019	0.01830[b]

[a]Ref. [5]

[b]Ref. [76]

Conclusion. Within the framework of the developed isotopic substitution theory in polyatomic molecules, isotopic relations between the main transformed dipole moment parameters of the overtones and combination bands were obtained for the first time for the XY_2-type molecules and their isotopologues (in particular for C_{2v} symmetry). These relations allow to predict the values of the corresponding transformed dipole moment parameters of various isotopologues on the basis of the available information on the parameters of the transformed dipole moment operator

of the "parent" molecule. These relations allow to avoid the difficulties associated with determining the partial pressure and simplify the line intensity analysis of isotopologues in times. This work is one of the stages in the development of the isotopic substitution theory applied for the line intensities calculation. At the moment, there are only relations for the first order parameters of the fundamental bands for XY_2 type molecules [7].

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